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February 02, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/542,088 ✓

FILING DATE: February 05, 2004 ✓

PRIORITY DOCUMENT

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17698 U.S. PTO

Practitioner's Docket No. U 015023-7

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: **ANDRÉ PETER STEYNBERG**

For: **CO-PRODUCTION OF HYDROCARBONS AND DIMETHYL ETHER**

Mail Stop Provisional Patent Application
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Optional Customer No. Bar Code



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PATENT TRADEMARK OFFICE

17354 U.S. PTO
60/542088



COVER SHEET FOR FILING PROVISIONAL APPLICATION
(37 C.F.R. § 1.51(c)(1))

WARNING: *"A provisional application must also include the cover sheet required by § 1.51(c)(1) or a cover letter identifying the application as a provisional application. Otherwise, the application will be treated as an application filed under paragraph (b) [nonprovisional application] of this section." 37 C.F.R. § 1.53(c)(1). See also M.P.E.P. § 201.04(b), 6th ed., rev. 3.*

CERTIFICATION UNDER 37 C.F.R. 1.10*

(Express Mail label number is mandatory.)

(Express Mail certification is optional.)

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on February 5, 2004, in an envelope as "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 Mailing Label Number EV 327552178 US addressed to the Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450.

CYNTHIA PADGETT

(type or print name of person mailing paper)

Cynthia Padgett

Signature of person mailing paper

WARNING: *Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.*

***WARNING:** *Each paper or fee filed by "Express Mail" must have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).*

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will not be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

NOTE: "A complete provisional application does not require claims since no examination on the merits will be given to a provisional application. However, provisional applications may be filed with one or more claims as part of the application. Nevertheless, no additional claim fee or multiple dependent claims fee will be required in a provisional application." Notice of December 5, 1994, 59 FR 63951, at 63953.

"Any claim filed with a provisional application will, of course, be considered part of the original provisional application disclosure." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

NOTE: "A provisional application is not entitled to the right of priority under 35 U.S.C. 119 or 365(a) or § 1.55, or to the benefit of an earlier filing date under 35 U.S.C. 120, 121 or 365(c) or § 1.78 of any other application. No claim for priority under § 1.78(a)(3) may be made in a design application based on a provisional application. No request under § 1.293 for a statutory invention registration may be filed in a provisional application. The requirements of §§ 1.821 through 1.825 regarding application disclosures containing nucleotide and/or amino acid sequences are not mandatory for provisional applications." 37 C.F.R. 1.53(c)(3).

NOTE: "No information disclosure statement may be filed in a provisional application." 37 C.F.R. § 1.51(d). "Any information disclosure statements filed in a provisional application would either be returned or disposed of at the convenience of the Office." Notice of December 5, 1994, 59 FR 63591, at 63594.

NOTE: "No amendment other than to make the provisional application comply with the patent statute and all applicable regulations, may be made to the provisional application after the filing date of the provisional application." 37 C.F.R. § 1.53(e).

NOTE: 35 U.S.C. 119(e) provides that "[i]f the day that is 12 months after the filing date of a provisional application falls on a Saturday, Sunday, or Federal Holiday within the District of Columbia, the period of pendency of the provisional application shall be extended to the next succeeding secular or business day."

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i).

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):
2. The name(s) of the inventor(s) is/are (37 C.F.R. § 1.51(c)(1)(ii)):

NOTE: "If the correct inventor or inventors are not named on filing, a provisional application without a cover sheet under § 1.51(c)(1), the later submission of a cover sheet under § 1.51(c)(1) during the pendency of the application will act to correct the earlier identification of inventorship." 37 C.F.R. § 1.48(f)(2).

NOTE: "The naming of inventors for obtaining a filing date for a provisional application is the same as for other applications. A provisional application filed with the inventors identified as 'Jones et al.' will not be accorded a filing date earlier than the date upon which the name of each inventor is supplied unless a petition with the fee set forth in § 1.17(i) is filed which sets forth the reasons the delay in supplying the names should be excused. Administrative oversight is an acceptable reason. It should be noted that for a 35 U.S.C. 111(a) application to be entitled to claim the benefit of the filing date of a provisional application the 35 U.S.C. 111(a)[.] application must have at least one inventor in common with the provisional application." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

The term "invention" is typically used to refer to subject matter which applicant is claiming in his/her application. Because claims are not required in a provisional application, it would not be appropriate to reference joint inventors as those who have made a contribution to the "invention" disclosed in the provisional application. If the "invention" has not been determined in the provisional application because no claims have been presented, then the name(s) of those person(s) who have made a contribution to the subject matter disclosed in the provisional application should be submitted. Section 1.45(c) states that "if multiple inventors are named in a provisional application, each named inventor must have made a contribution, individually or jointly, to the subject matter disclosed in the provisional application." All that § 1.45(e) requires is that if someone is named as an inventor, that person must have made a contribution to the subject matter disclosed in the provisional application. When applicant has determined what the invention is by the filing of the 35 U.S.C. 111(a) application, that is the time when the correct inventors must be named. The 35 U.S.C. 111(a) application must have an inventor in common with the provisional application in order for the 35 U.S.C. 111(a) application to be entitled to claim the benefit of the provisional application under 35 U.S.C. 119(e). Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,208.

See 37 C.F.R. § 1.53.

1.	<u>ANDRÉ</u>	<u>PETER</u>	<u>STEYNBERG</u>
	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME
2.	<u>PIERRE</u>		<u>GREEFF</u>
	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME
3.			
	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME

3. Residence address(es) of the inventor(s), as numbered above (37 C.F.R. § 1.51(c)(1)(iii)):

1. 3 ORANGE RIVER STREET, SE4, VANDERBIJLPARK, 1911, REPUBLIC OF SOUTH AFRICA
2. 108 6TH STREET, LINDEN, JOHANNESBURG, 2195, REPUBLIC OF SOUTH AFRICA
3. _____

4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

HYDROCARBON SYNTHESIS

5. The name, registration, customer and telephone numbers of the practitioner (if applicable) are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: CLIFFORD J. MASS
 Reg. No. 30,086
 Customer No. 00140

Tel. (212) 708-1890

(complete the following, if applicable)

☐ A power of attorney accompanies this cover sheet.

6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. U 015023-7

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

Ladas & Parry, 26 West 61st Street, New York, NY 10023

8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was made by an agency of the United States Government, or under contract with an agency of the United States Government.

☒ No
☐ Yes

The name of the U.S. Government agency and the Government contract number are:

9. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. §§ 1.51(c)(2)-(3):

Specification:	No. of pages <u>18</u>
Drawings:	No. of sheets <u>2</u>

B. Additional documents:

☐ Claims: No. of claims

Note: See 37 C.F.R. § 1.51.

☐ Power of attorney
☐ Small Entity Statement or Written Assertion
☐ Assignment
☐ English language translation of non-English provisional application and Statement of Accuracy thereof

NOTE: A provisional application which is filed in a language other than English, does not have to have an English language translation. See 37 C.F.R. § 1.52(d)(2). However, if the provisional application is not in the English language and will later serve as a benefit of its filing date for a nonprovisional application, other than a design patent, or for an international application designating the U.S., then an English language translation must be filed in the provisional application or the later filed nonprovisional application. See § 1.78(a)(5)(iv).

10. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00, for other than a small entity, and \$80.00, for a small entity.

- ☒ Applicant is not a small entity.
☐ Applicant is a small entity.

NOTE: "A . . . statement i compliance with existing § 1.27 is required to be filed in each provisional application in which it is desired to pay reduced fees." Notice of April 14, 1995, 60 Fed. Reg. 20, 195, at 20,197.

11. Small entity assertion

- ☐ A Statement or Written Assertion that this is a filing by a small entity under 37 C.F.R. § 1.27(c)(1) is attached.
☐ Small entity status is asserted for this application by payment of the small entity filing fee under § 1.16(k). 37 C.F.R. § 1.27(c)(3).

***WARNING:** "Small entity status must not be established unless the person or persons signing the . . . statement can unequivocally make the required self-certification." M.P.E.P. Section 509.03, 6th ed., rev. 2, July 1996 (emphasis added).*

12. Fee payment

- ☒ Fee payment in the amount of \$ 160.00 is being made at this time.
☐ No filing fee is to be paid at this time. (This and the surcharge required by 37 C.F.R. § 1.16(l) can be paid subsequently.)

13. Method of fee payment

☒ Check in the amount of \$ 160.00.
☐ Charge Account No. 12-0425, in the amount of \$ _____.
A duplicate of this Cover Sheet is attached.

Please charge Account No. 12-0425 for any deficiency in the fee paid.

Date: _____

Signature of submitter

Tel.: ()

OR

Date: February 5, 2004

Signature of practitioner

Reg. No.: 30,086

CLIFFORD J. MASS
(type or print name of practitioner)

Tel.: (212)708-1890

LADAS & PARRY
P.O. Address

Customer No.: 00140

26 WEST 61ST STREET
NEW YORK, NEW YORK 10023

UNITED STATES OF AMERICA

SPECIFICATION

TO ALL WHOM IT MAY CONCERN, BE IT KNOWN THAT:

**STEYNBERG, André Peter
GREEFF, Pierre**

have invented a certain

"CO-PRODUCTION OF HYDROCARBONS AND DIMETHYL ETHER"

of which the following is a specification

.1

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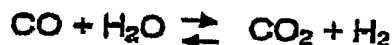
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Typically, the Fischer-Tropsch reaction stage includes a slurry bed of a solid particulate Fischer-Tropsch catalyst suspended in a carrier liquid, with the gaseous feedstock entering the slurry bed at a low level.

5 The Fischer-Tropsch catalyst used in the Fischer-Tropsch reaction stage may be a shifting catalyst, e.g. an iron catalyst, and is preferably a promoted iron catalyst. The catalyst may be promoted for activity and/or selectivity.

10 By "shifting catalyst" is meant a hydrocarbon synthesis catalyst which, at the operating conditions of the Fischer-Tropsch reaction stage, converts more than 2 % of CO passing through the reaction stage into CO₂ by the water-gas shift reaction:



5 When employing a slurry bed in the Fischer-Tropsch reaction stage, the hydrogen and carbon monoxide react catalytically as they pass upwardly through the slurry bed, thereby to form liquid hydrocarbon products and gaseous products, with the liquid hydrocarbon products thus constituting the carrier liquid of the slurry bed.

) The process typically includes withdrawing liquid hydrocarbon products and gases and vapours from the Fischer-Tropsch reaction stage, cooling the gases and vapours to condense liquid hydrocarbons and reaction water present therein and to obtain the tail gas comprising the unreacted hydrogen and carbon monoxide. Typically, the condensed liquid hydrocarbons, reaction water and tail gas are separated in, and withdrawn from, a separator vessel, with the composition of at least a portion of the tail gas then being adjusted to provide the DME synthesis feedstock with the desired syngas number.

The tail gas from the Fischer-Tropsch reaction stage thus typically includes unreacted hydrogen, unreacted carbon monoxide and gaseous products which are formed in the Fischer-Tropsch reaction stage, including CO₂, and which have not been condensed and separated from the tail gas. This tail gas typically includes small quantities of C₅- hydrocarbons. Thus carbon dioxide will be formed in the Fischer-Tropsch reaction stage by the water-gas shift reaction.

Preferably, the syngas number is between 1.85 and 2.15, more preferably between 1.9 and 2.1, e.g. about 2.

Advantageously, it is expected that the DME synthesis feedstock may include light hydrocarbons from the Fischer-Tropsch reaction stage, without the presence of the light hydrocarbons adversely affecting the DME synthesis, thus obviating the need substantially entirely to remove these light hydrocarbons from the tail gas obtained from the Fischer-Tropsch reaction stage.

Adjusting the composition of at least a portion of the tail gas may include removing some CO_2 from said portion of the tail gas. Thus, the syngas number may be adjusted upwardly. As will be appreciated, the gaseous feedstock can be derived from a methane-containing gas such as natural gas, or it can be derived from solid carbonaceous material such as coal. When the gaseous feedstock is derived from a carbonaceous material, such as coal, it is expected that, in a preferred embodiment of the process, CO_2 will be removed from said portion of the tail gas. In an optional embodiment of the invention CO_2 is removed from said portion of the tail gas when the gaseous feedstock is derived from a methane-containing gas. Preferably, this is effected without compressing said portion of the tail gas.

Removing some CO_2 from said portion of the tail gas may include absorbing the CO_2 in a solvent, e.g. a Benfield solution. The process may thus also include recovering the removed CO_2 , by stripping the CO_2 from the solvent. This may be achieved, for example, by using a stripping gas and elevating the temperature of the solvent.

In one embodiment of the invention, the stripping gas used to recover CO_2 from said portion of the tail gas is methane-containing gas from which the gaseous feedstock is derived.

Instead, or in addition, adjusting the composition of at least a portion of the tail gas may include adding an H_2 -rich gas to said portion of the tail gas.

Adding an H₂-rich gas to said portion of the tail gas may include reforming a portion of the gaseous feedstock in a steam reforming stage to produce an H₂ rich reformed gas, and combining at least some of the H₂ rich reformed gas with said portion of the tail gas to provide the DME synthesis feedstock.

Typically, an installation for synthesising hydrocarbons which employs a Fischer-Tropsch synthesis stage includes a hydroprocessing facility, which in turn relies on a steam reforming facility to generate H₂ for hydroprocessing. Advantageously, the process of the invention can thus rely on such a steam reforming facility, possibly upgraded if necessary, also to provide the H₂ rich reformed gas with which the composition of said portion of the tail gas can be adjusted.

The process may include recycling some of the tail gas to the Fischer-Tropsch reaction stage. The tail gas recycle may be used to increase overall Fischer-Tropsch reaction stage CO and H₂ conversion to a value of up to 60 %, preferably to a value of up to about 50 %. The CO and H₂ per pass conversion is in the order of about 30 %. It is known that a reaction stage using promoted iron Fischer-Tropsch catalyst suffers from a rapid decline in reaction stage productivity as the per pass conversion of CO and H₂ increases. It is thus advantageous that the Fischer-Tropsch reaction stage may be operated with a low per pass conversion of CO and H₂ of between about 30 % and about 50 %, preferably about 30 %.

The gaseous feedstock to tail gas recycle ratio will typically be about 1 : 1, but may vary depending on the gaseous feedstock composition.

The Fischer-Tropsch reaction stage may operate at a temperature of less than 280 °C. Typically, the Fischer-Tropsch reaction stage operates at a temperature of between 160 °C and 280 °C, preferably between 220 °C and 260 °C, e.g. about 240 °C. The Fischer-Tropsch reaction stage is thus a high chain growth, typically slurry bed, reaction stage, operating at a predetermined operating pressure in the range 10 to 50 bar, e.g. about 40 bar.

The process of the invention may include treating the hydrocarbons to provide a naphtha fraction and/or a kerosene fraction, e.g. a C₅ to a C₈ or C₉ naphtha

cut or fraction and a C_9 or C_{10} to C_{13} or C_{14} kerosene cut or fraction. Preferably, lubricating oils and diesel are also produced. In fact, the liquid hydrocarbon product from the Fischer-Tropsch reaction stage may comprise predominantly wax. In other words, at least about 50 % by mass of the liquid hydrocarbon product from the Fischer-Tropsch reaction stage may be made up of $C_{15}+$ hydrocarbons. This wax may be processed in a wax processing or hydroprocessing stage to give high yields of high quality lubricant base oil products and/or high value wax products. The wax processing stage may also yield a portion of the naphtha fraction, e.g. a C_5 to C_{10} naphtha fraction.

A kerosene fraction, e.g. a C_9 to C_{13} fraction of the condensed liquid hydrocarbons from the Fischer-Tropsch reaction stage may be treated to remove oxygenated hydrocarbons and then alkylated and subjected to a separation stage to produce linear alkyl benzene, and optionally paraffins and oxygenates. The naphtha fraction may be processed to extract olefin comonomers such as 1-hexene and 1-octene, and optionally paraffins and oxygenates.

As mentioned hereinbefore, the gaseous feedstock may be derived from a methane-containing gas. Derivation of the gaseous feedstock may include reforming the methane-containing gas in a reforming stage in the presence of oxygen and steam. The reforming stage may be an autothermal reforming stage. Preferably, a low steam to carbon ratio of between about 0.2 and about 0.6, e.g. about 0.4, is used in the autothermal reforming stage. Instead, the reforming stage may be a catalytic or a non-catalytic partial oxidation stage, in which a steam to carbon ratio of 0.2 or less is typically used.

When derived from a methane-containing gas, the gaseous feedstock may comprise hydrogen and carbon monoxide in a molar ratio of between about 2.1 and about 2.3. Thus there is an excess of H_2 above the stoichiometric requirements for hydrocarbon synthesis. When derived from a solid carbonaceous material, and relying on gasification of the solid carbonaceous material in a gasification stage, the carbonaceous feedstock typically has an H_2/CO molar ratio of between about 0.7 and about 2.1, often between 0.7 and 2.0. Thus there may be a deficit of the H_2 compared to the stoichiometric requirement for hydrocarbon synthesis.

Converting at least a portion of the DME synthesis feedstock fed to the DME synthesis stage to DME may include contacting the DME synthesis feedstock with a methanol catalyst and a methanol dehydration catalyst, thereby to produce DME. As methanol catalyst, a copper-containing catalyst is usually employed. Suitable catalysts however include compositions containing copper, zinc oxide, chromia and/or alumina and possibly other oxidic materials such as magnesia. The DME synthesis stage will typically require recycle of unreacted DME synthesis feedstock to obtain satisfactory conversion.

The produced methanol may simultaneously be dehydrated to produce the DME. Typically, a product mixture with a high DME to methanol ratio is produced, which can be subjected to a rectification process to recover a DME product with the required purity. Separated methanol may be recycled to the DME synthesis stage. Thus, DME is produced directly in combination with methanol by a combined synthesis from the DME feedstock by use of catalyst active in both the synthesis of methanol from synthesis gas and methanol dehydration. Methanol dehydration catalysts usually comprise alumina or alumina silicates as active compounds.

According to another aspect of the invention, there is provided a process for co-producing a liquid fuel and light olefins, the process including co-producing liquid hydrocarbons and dimethyl ether (DME) from a gaseous feedstock comprising hydrogen and carbon monoxide; treating the liquid hydrocarbons to provide a liquid fuel; and converting at least some of the DME into light olefins.

The liquid hydrocarbons and the DME may be co-produced in accordance with the process in accordance with the first aspect of the invention. Advantageously, the DME being converted into light olefins need not be of high purity.

Treating the liquid hydrocarbons may include subjecting at least a portion of the liquid hydrocarbons to hydroprocessing, thereby to produce lubricants and a diesel fraction, the liquid fuel produced thus being Fischer-Tropsch derived liquid fuel and including a diesel fraction.

Treating the liquid hydrocarbons may also include producing a naphtha fraction and optionally a kerosene fraction, and converting at least some of the naphtha fraction and optionally some of the kerosene fraction with at least some of the DME into light olefins, such as ethylene and propylene. Preferably, a zeolite such as ZSM-5 or a molecular sieve catalyst, preferably a silicoalumino phosphate catalyst is used to convert the DME and a naphtha fraction and optionally a kerosene fraction into light olefins. Suitable silicoalumino phosphate catalysts include SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47 and SAPO-56, the metal-containing forms thereof, and mixtures thereof.

The invention will now be described, by way of example, with reference to the two accompanying diagrammatic drawings in which

Figure 1 shows a simplified flow sheet of a process in accordance with the invention for co-producing hydrocarbons, DME and light olefins; and

Figure 2 shows a simplified flow sheet of another embodiment of the process in accordance with the invention for co-producing hydrocarbons, DME and light olefins.

Referring to Figure 1 of the drawings, reference numeral 10 generally indicates a process in accordance with the invention for co-producing hydrocarbons such as Fischer-Tropsch derived lubricating oils and diesel, DME and light olefins such as ethylene and propylene.

The process 10 includes an autothermal reforming stage 12 provided with a natural gas feedstock line 14 and oxygen and steam feed lines 16, 18. The autothermal reforming stage 12 is connected to a Fischer-Tropsch reaction stage 20 by means of a syngas feed line 22. A gaseous product line 24 leads from the Fischer-Tropsch reaction stage 20 to an air cooler 26 and from the air cooler 26 to a three-phase separation stage 28. An aqueous condensate line 32 leads from the three-phase separation stage 28, a tail gas line 34 leads to an optional light hydrocarbon recovery stage 36 and a hydrocarbon condensate line 38 leads to a fractionation stage 40. From the fractionation stage 40 a naphtha fraction line 30 leads to an optional comonomer separation stage 56, a kerosene fraction line 42 leads to an alkylation stage 44, a

heavies line 46 leads to a hydroprocessing stage 48, a diesel fraction line 50 leads to a diesel hydrotreating stage 52, and a light hydrocarbon line 84 is provided.

5 The optional comonomer stage 56 is connected to the light hydrocarbon line 84 from the fractionation stage 40 with a naphtha line 57. Comonomer product lines 60 (only one of which is shown) for comonomer product such as 1-hexene and 1-octene lead from the optional comonomer stage 56.

10 The optional alkylation stage 44 is provided with a benzene feed line 54 and is connected to the diesel hydrotreating stage 52 by a paraffins/oxygenates feed line 58. A linear alkyl benzene product line 62 also leads from the optional alkylation stage 44.

5 The Fischer-Tropsch reaction stage 20 is connected to the hydroprocessing stage 48 by means of a liquid hydrocarbon line 64. A naphtha line 66 from the hydroprocessing stage 48 joins the light hydrocarbon line 84 from the fractionation stage 40 and a diesel line 70 from the hydroprocessing stage 48 joins a diesel line 72 from the diesel hydrotreating stage 52. An unconverted heavies line 74 from the hydroprocessing stage 48 is recycled to extinction to the hydroprocessing stage 48. A lubricating oils product line 82 leads from the hydroprocessing stage 48.

A tail gas recycle line 86 and a compressor 88 are provided to recycle tail gas from the three-phase separation stage 28 to the Fischer-Tropsch reaction stage 20.

The process 10 further includes a steam reforming stage 90 also fed by the natural gas feedstock line 14. From the steam reforming stage 90, a hydrogen rich gas line 92 leads and branches to feed into an optional water-gas shift reaction stage 94, and optionally to a DME synthesis stage 98. The steam reforming stage 90 is provided with a steam feed line 100 and the optional water-gas shift reaction stage 94 is provided with a steam feed line 102.

The process 10 further includes a pressure swing adsorption stag 104 which receives gas, either from the water-gas shift reaction stage 94 or the steam reforming stage 90 if the wat r-gas shift reaction stage 94 is not present, by means of a gas feed line 106. From the pressure swing adsorption stage 104, a hydrogen line 108

leads to the hydroprocessing stage 48, and a fuel gas line 110 is provided. A hydrogen line 109 leads from the hydrogen line 108 to the diesel hydrotreating stage 52.

5 The optional CO₂ separation stage 96 is optionally connected to the light hydrocarbon recovery stage 36 by means of a line 112, which may instead feed into the DME synthesis stage 98. A compressor 97 may be required to increase the pressure to a suitable pressure for DME synthesis. The natural gas feedstock line 14 also branches to the optional CO₂ separation stage 96.

10 The optional CO₂ separation stage 96 is provided with a CO₂ enriched gas line 114 which is either vented or at least partly returned to the autothermal reforming stage 12. A CO₂ lean gas line 116 leads to the DME synthesis stage 98.

5 From the DME synthesis stage 98, an aqueous condensate line 118, a tail gas line 120 and a DME product line 122 lead. The tail gas line 120 leads into an optional light hydrocarbon recovery stage 124 from where a light hydrocarbon line 126 joins the DME product line 122 and a fuel gas line 128 is provided, which optionally returns to the pressure swing adsorption stage 104.

) The DME product line 122 is also joined by the light hydrocarbon line 84, after the light hydrocarbon line 84 is joined by a light hydrocarbon line 130 from the optional light hydrocarbon recovery stage 36. The DME product line 122 feeds into a light olefins production stage 132 from where an aqueous condensate line 134 and a light olefins product line 136 lead.

In use, the process 10 is provided with a methane rich gas, such as natural gas, fed along the natural gas feedstock line 14. In the autothermal reforming stage 12, the natural gas is reformed in the presence of oxygen and steam and at a pressure of about 55 bar and a temperature of about 1050 °C. Typically, the steam is generated at a pressure of between about 60 bar and about 120 bar, by indirect heat exchange (not shown) with the autothermal reforming stage 12 hot outlet stream before the synthesis gas is removed by means of the line 22. Preferably, a low steam/carbon ratio of 0.4 is employed in the autothermal reforming stage 12 to produce a synthesis gas with an H₂/CO ratio in the range of about 2.1 to 2.3, ie slightly rich in hydrogen. The synthesis

gas thus comprises primarily carbon monoxide, carbon dioxide and hydrogen and includes residual methane and typically small amounts of light paraffins, such as methane and propane.

5 The synthesis gas is fed from the autothermal reforming stage 12 to the Fischer-Tropsch reaction stage 20 by means of the syngas feed line 22. Although not shown in the drawings, the synthesis gas is typically first cooled in an air cooler to a temperature of about 70°C, before being fed into the Fischer-Tropsch reaction stage 20. During this air cooling of the synthesis gas, an aqueous condensate is produced, which
10 is removed from the synthesis gas.

The Fischer-Tropsch reaction stage 20 comprises one or more slurry phase reactors, operating at a pressure between 10 bar and 50 bar, typically about 40 bar and a temperature typically between 220°C and 260°C. These three-phase slurry phase
5 reactors each include a slurry bed of solid particulate promoted iron Fischer-Tropsch catalyst suspended in liquid hydrocarbon product (mostly wax). The synthesis gas enters the slurry beds at a low level and the hydrogen and carbon monoxide react catalytically as they pass upwardly through each slurry bed, thereby to form liquid hydrocarbon products and gaseous products. The liquid product is withdrawn along the
10 liquid hydrocarbon line 64 and fed to the hydroprocessing stage 48. The gaseous products and unreacted synthesis gas feedstock leave the Fischer-Tropsch reaction stage 20 along the gaseous product line 24. In the air cooler 26 the gaseous products and unreacted feedstock are cooled, producing an aqueous condensate which is removed along the aqueous condensate line 32, from the three-phase separation stage 28 where it is separated. A hydrocarbon condensate is removed by means of the hydrocarbon condensate line 38 from the separation stage 28 and fed to the fractionation stage 40. The three-phase separation stage 28 also produces a tail gas which is withdrawn along the tail gas line 34.

A portion of the tail gas is recycled by means of the tail gas recycle line 86 and the compressor 88 to the Fischer-Tropsch reaction stage 20. A ratio of recycled tail gas to fresh synthesis gas of about 1 : 1 is maintained. In the Fischer-Tropsch reaction stage 20, overall CO and hydrogen conversion is maintained at about 50 %. Per pass conversion is thus about 30 %. This is advantageous, as water is formed in the Fischer-

Tropsch reaction stage 20 and water deactivates the iron catalyst. Thus, by keeping the per pass conversion low, the partial pressure of the water is kept sufficiently low, ie less than 3 bar, to ensure that the catalyst activity remains at a reasonably high level.

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A portion of the tail gas from the three-phase separation stage 28 is fed to the DME synthesis stage 98 by means of the line 112, possibly being compressed by the compressor 97. Before entering the DME synthesis stage 98, this portion of tail gas may however be subjected to a light hydrocarbon recovery operation in the optional light hydrocarbon recovery stage 36, in order to recover light hydrocarbons such as C₂ to C₅ hydrocarbons and traces of C₆ hydrocarbons, which may then be removed along the light hydrocarbon line 130.

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The portion of the tail gas fed to the DME synthesis stage typically has a syngas number which is less than 2 because of the presence of excess CO₂. Preferably, for DME synthesis, the syngas number should be about 2 and it is thus desirable that the composition of the tail gas be adjusted prior to the tail gas entering the DME synthesis stage 98. The composition of the tail gas can be adjusted by either removing excess CO₂ or adding a hydrogen-rich gas to the tail gas.

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In the process 10 shown in Figure 1 of the drawings, the composition of the tail gas can be adjusted for DME synthesis purposes by the removal of CO₂. This option is illustrated by the CO₂ separation stage 96 into which the portion of the tail gas intended for DME synthesis is fed by means of the line 112 between the light hydrocarbon recovery stage 36 and the CO₂ separation stage 96. In the CO₂ separation stage 96, the tail gas is contacted with a solvent, such as a Benfield solution, which absorbs some of the CO₂, providing a CO₂ lean gas which can be fed by means of the CO₂ lean gas line 116 to the DME synthesis stage 98.

The CO₂ removed from the tail gas may be recovered by stripping it from the solvent. Typically, this is achieved by using a stripping gas (in this case the natural gas feedstock) and elevating the temperature of the solvent, producing a CO₂ rich gas.

By means of the CO₂ rich gas line 114, the CO₂ rich gas is either vented or at least partly recycled to the autothermal reforming stage 12. This recycle facility allows for

better control of the H_2/CO ratio in the synthesis gas fed to the reaction stage 20 thereby favourably to decrease methane selectivity in the Fischer-Tropsch reaction stage 20.

5 As mentioned hereinbefore, another option available to adjust the syngas number of the DME synthesis feedstock is to add a hydrogen rich gas to the DME synthesis feedstock. This option can easily be entertained when the steam reforming stage 90 is present and is illustrated by means of the H_2 rich gas line 92 joining the line 112 between the light hydrocarbon recovery stage 36 and the DME synthesis stage 98.

10 The hydrogen rich gas is obtained from the steam reforming stage 90, which is fed with natural gas along the natural gas feedstock line 14 and with high pressure steam by means of the steam feed line 100. In the steam reforming stage 90, the methane-containing natural gas and the steam are mixed and passed at an elevated temperature and pressure, through externally heated tubes containing a suitable steam reforming catalyst. Catalysts employed are typically nickel on a suitable support, e.g. alumina, 5 magnesia, zirconia, or calcium-aluminate cement. The tubes are heated by a suitable gas, typically the product of combusting a fuel gas. Typically, the temperature is in the range of 700 °C to 950 °C, and the pressure is in the range of 15 to 50 bar, particularly 40 bar. The steam is normally present in an excess over that required for the reforming reaction in order to reduce the risk of formation of carbon deposits on the reforming catalyst. The reformed gas will contain hydrogen, carbon monoxide, carbon dioxide, unreacted steam and methane. Although not shown in Figure 1 of the drawings, the reformed gas is usually cooled to below the dew point of the steam therein to condense the unreacted steam which is then separated, leaving the residual reformed gas which is a hydrogen rich gas.

For some operations, a gas even more rich in hydrogen than the H_2 rich or reformed gas from the steam reforming stage 90 is required. This gas can be obtained by subjecting the H_2 rich or reformed gas to a water-gas shift reaction, as is illustrated by the water-gas shift reaction stage 94. In the water-gas shift reaction stage 94, the H_2 rich gas is mixed with steam fed by means of the steam feed line 102 and passed over a suitable shifting catalyst which promotes the water-gas shift reaction. Some of the carbon monoxide and steam is thus converted to carbon dioxide and hydrogen, thereby

further enriching the H_2 rich gas in hydrogen. This further enriched gas is fed by means of the gas feed line 106 into the pressure swing adsorption stage 104 where by means of conventional pressure swing adsorption a hydrogen stream is produced which can be fed by means of the hydrogen line 108 to the hydroprocessing stage 48 and by means of the hydrogen line 109 to the diesel hydrotreating stage 52. A fuel gas produced by the pressure swing adsorption stage 104 is removed by means of the fuel gas line 110. This fuel gas can be used for heating purposes in other areas of the process 10, e.g. the steam reforming stage 90.

In the DME synthesis stage 98, the DME synthesis feedstock is converted to DME by passing the DME synthesis feedstock over a methanol catalyst and a methanol dehydration catalyst, providing a product mixture with a high DME to methanol ratio. The product mixture is rectified to the required purity and the excess methanol is recycled. The DME synthesis stage 98 is preferably operated at a pressure of at least 25 bar preferably above 35 bar and a temperature as low as economically feasible, to promote methanol formation and methanol dehydration. As mentioned hereinbefore, it may be necessary to compress the DME synthesis feedstock, by means of the compressor 97, before passing the DME synthesis feedstock to the DME synthesis stage 98. Typically, a copper-containing catalyst is used to produce methanol from the DME synthesis feedstock, whereas the methanol dehydration catalyst is typically a catalyst comprising alumina or alumina silicates as active compounds.

Advantageously, the DME product can be converted to light olefins in the light olefins production stage 132. The DME product is thus fed to the light olefins production stage 132 by means of the DME product line 122 and passed over a DME dehydration catalyst, such as ZSM-5 or SAPO-34. In the process, the DME is dehydrated, producing an aqueous condensate stream which is removed along the aqueous condensate line 134, and a light olefins product which is removed along the light olefins product line 136. This light olefins product typically includes ethylene and propylene and small amounts of aromatics.

A tail gas from the DME synthesis stage 98 is fed by means of the tail gas line 120 into an optional light hydrocarbon recovery stage 124 to recover at least C_3+ light hydrocarbons, which are combined with the DME product in the DME product line

122, by means of the light hydrocarbon line 126, for conversion to light olefins in the light olefins production stage 132. The light hydrocarbon recovery stage 124 also produces a fuel gas, which is removed along the fuel gas line 128 for use in other locations, or which is optionally recycled to the pressure swing absorption stage 104 by means of the fuel gas line 128.

The hydrocarbon condensate removed from the three-phase separation stage 28 by means of the hydrocarbon condensate line 38 is subjected to fractionation in a fractionation stage 40 (atmospheric distillation) to produce a heavies stream which is passed to the hydroprocessing stage 48 by means of the heavies lines 46, a diesel fraction which is fed to the diesel hydrotreating stage 52 by means of the diesel fraction line 50 and a light hydrocarbon fraction which is fed to the light olefins production stage 132 by means of the light hydrocarbon line 84. A kerosene fraction, e.g. a C₁₀ to C₁₄ fraction, is removed from the fractionation stage 40 by means of the kerosene fraction line 42 and fed to the alkylation stage 44, where it is treated to remove oxygenated hydrocarbons and then alkylated in the presence of benzene to produce a linear alkyl benzene product. The benzene is fed by means of the benzene feed line 54 into the alkylation stage 44 and a paraffin/oxygenates mixture is removed by means of the paraffin/oxygenates feed line 58, which is fed into the diesel hydrotreating stage 52. Linear alkyl benzene product is removed by means of the linear alkyl benzene product line 62 from the alkylation stage 44.

A naphtha fraction, e.g. a C₅ to C₈ or C₉ fraction is removed from the fractionation stage 40 by means of the naphtha fraction line 30 and fed to a comonomer separation stage 56 from which comonomer products, e.g. 1-hexene and 1-octene (C₆ and C₈ alpha olefins), are removed by means of comonomer product lines 60 (only one of which is shown). The remaining naphtha is fed to the light hydrocarbon line 84 by means of the naphtha line 57.

In the diesel hydrotreating stage 52, the diesel fraction from the fractionation stage 40 and the paraffins and oxygenates remaining after the alkylation stage 44 are subjected to hydrotreatment, with the hydrogen being fed by means of the line 109 from the pressure swing adsorption stage 104. A diesel product is thus produced from

paraffins, olefins and oxygenates and removed from the diesel hydrotreating stage 52 by means of the diesel line 72.

In the hydroprocessing stage 48, the liquid hydrocarbon wax from the Fischer-Tropsch reaction stage 20 and the heavy hydrocarbons from the fractionation stage 40 are subjected to hydroprocessing. The hydrogen is fed from the pressure swing adsorption stage 104 by means of the hydrogen line 108 into the hydroprocessing stage 48. The hydroprocessing stage 48 produces a naphtha product which is removed by means of the naphtha line 66 and sent to the light olefins production stage 132. A diesel product from the hydroprocessing stage 48 is removed by means of the diesel line 70. Unconverted heavies from the hydroprocessing stage 48 is removed by means of the unconverted heavies line 74 and recycled. The hydroprocessing stage 48 produces a range of valuable lubricating oils and other waxes and products, which are represented by the lubricating oils product line 82.

Referring to Figure 2 of the drawings, a process in accordance with the invention for producing liquid hydrocarbon fuels, DME and light olefins, is generally indicated by reference numeral 200. The process 200 is similar to the process 10, and unless otherwise indicated, the same reference numerals are used to indicate the same or similar parts or features. The process 200 illustrates the invention for the case where the gaseous feedstock is derived from a solid carbonaceous material, such as coal.

The process 200 includes a gasification stage 202 supplied with a coal feedstock, indicated by reference numeral 204. A raw gas line 206 connects the gasification stage 202 to a CO₂ and sulphur removal stage 208 from where the syngas feed line 22 leads into the Fischer-Tropsch reaction stage 20.

As will be noted in Figure 2, the light hydrocarbon recovery stage 36 is optionally followed by a slipstream water-gas shift reaction stage 94, which is thus optionally located between the light hydrocarbon recovery stage 36 and the CO₂ separation stage 96. A CO₂ gas line 210 leads from the CO₂ separation stage 96.

The process 200 is operated in similar fashion to the process 10, but with a few alterations. Instead of a methane-containing gas providing the hydrocarbon

feedstock, the hydrocarbon feedstock is derived from coal which is fed to the gasification stage 202 and gasified in a plurality of conventional gasifiers, such as Lurgi (trade name) gasifiers. The gasifiers typically produce a gaseous carbonaceous feedstock with an H_2/CO molar ratio of between about 0.7 and about 2.1, more typically between about 1.9 and 2.1 when Lurgi (trade name) gasifiers are being used. The raw gas from the gasification stage 202 is fed by means of the raw gas line 206 to the CO_2 and sulphur removal stage 208 to produce a synthesis gas suitable for Fischer-Tropsch hydrocarbon synthesis. The synthesis gas is then fed by means of the synthesis gas feed line 22 into the Fischer-Tropsch reaction stage 20 from where the process 200 is very similar to the process 10 in respect of the stages 26, 28, 40, 44, 48, 56, 52, 36, 98, 124 and 132. However, the optional slip-stream water-gas shift reaction stage 94 is provided after the light hydrocarbon recovery stage 36 with the purpose of enriching the tail gas being fed to the DME synthesis stage 98 with hydrogen. Thus, in the water-gas shift reaction stage 94, carbon monoxide is reacted with steam to produce carbon dioxide and hydrogen, whereafter some of the carbon dioxide is removed in the CO_2 separation stage 96 to produce a carbon dioxide stream indicated by reference numeral 210 and a CO_2 lean gas, which is in effect hydrogen enriched, and which is combined by means of the CO_2 lean gas line 116 with the tail gas in the line 112 between the light hydrocarbons recovery stage 36 and the DME synthesis stage 98 to provide a DME synthesis feedstock with a syngas number of about 2.

It is an advantage of the process 10, 200, that DME, naphtha and LPG are co-processed to produce light olefins such as ethylene and propylene. The process 10, as illustrated, is also quite flexible as far as the relative production of Fischer-Tropsch hydrocarbons and DME or light olefins is concerned, with the production of one versus the production of the other easily being increased or decreased, depending on where most value can be derived from. The process also allows for conversion of some of the CO_2 produced by synthesis gas production and Fischer-Tropsch reaction to useful products by means of DME synthesis if hydrogen is available. Overall carbon efficiency is thus improved and CO_2 emissions reduced. Furthermore, if the DME synthesis can be effected economically at a pressure similar to but lower than the pressure at which the Fischer-Tropsch reaction stage 20 is operated, no additional compression of the tail gas is required for DME synthesis purposes. The processes 10, 200, as illustrated, also allow less severe light hydrocarbon recovery in the light hydrocarbon recovery stage 36,

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than is the case for a conventional Fischer-Tropsch synthesis process aimed only at producing Fischer-Tropsch derived hydrocarbons, if the light hydrocarbons can be fed through the DME synthesis stage 98 without adverse effects. The process 10, 200, as illustrated, enjoys the benefits of Fe-based Fischer-Tropsch catalysts, whilst simultaneously, as a result of the DME synthesis stage, avoiding the disadvantages of using Fe-based Fischer-Tropsch catalysts.

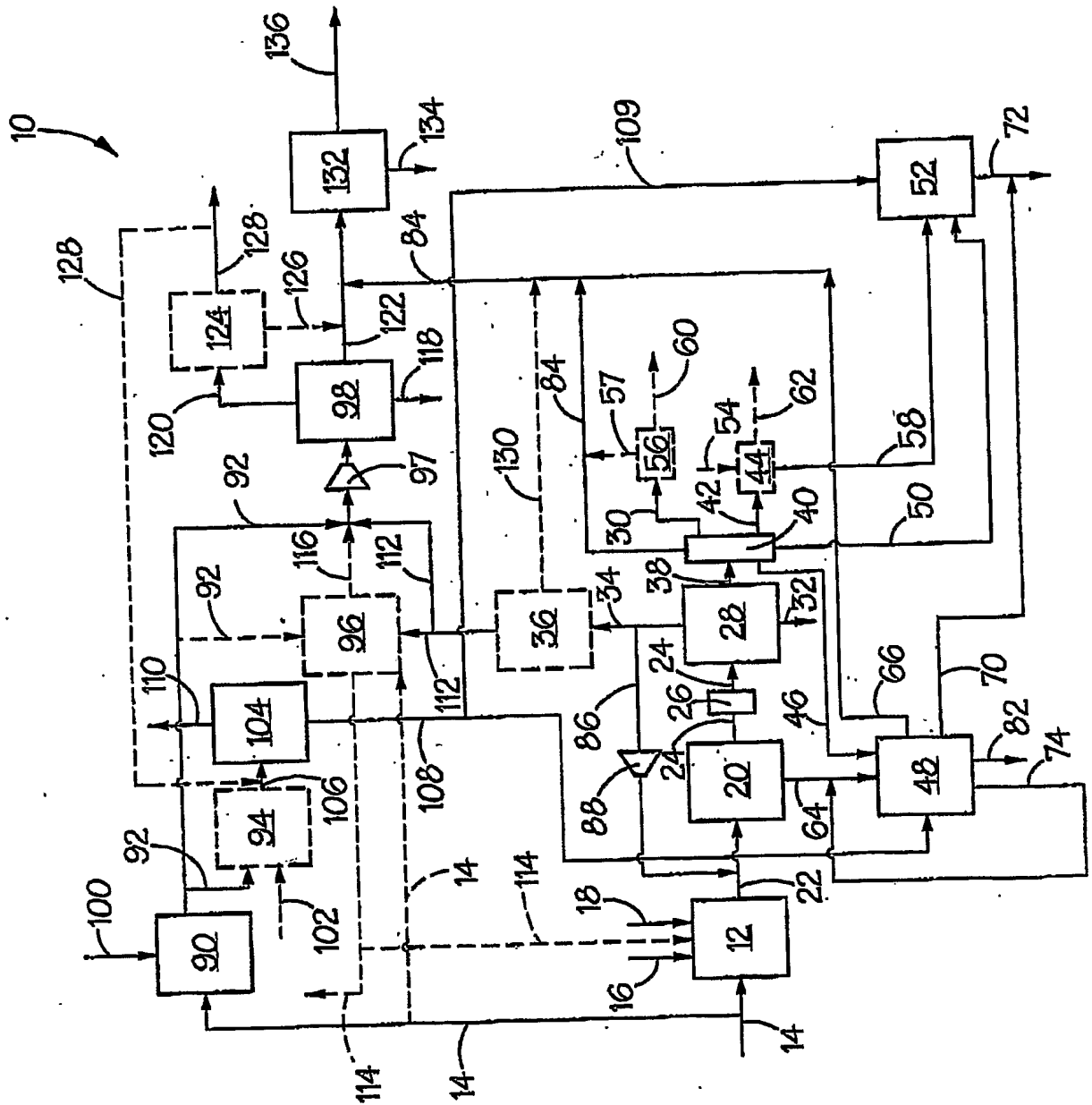


Fig 1

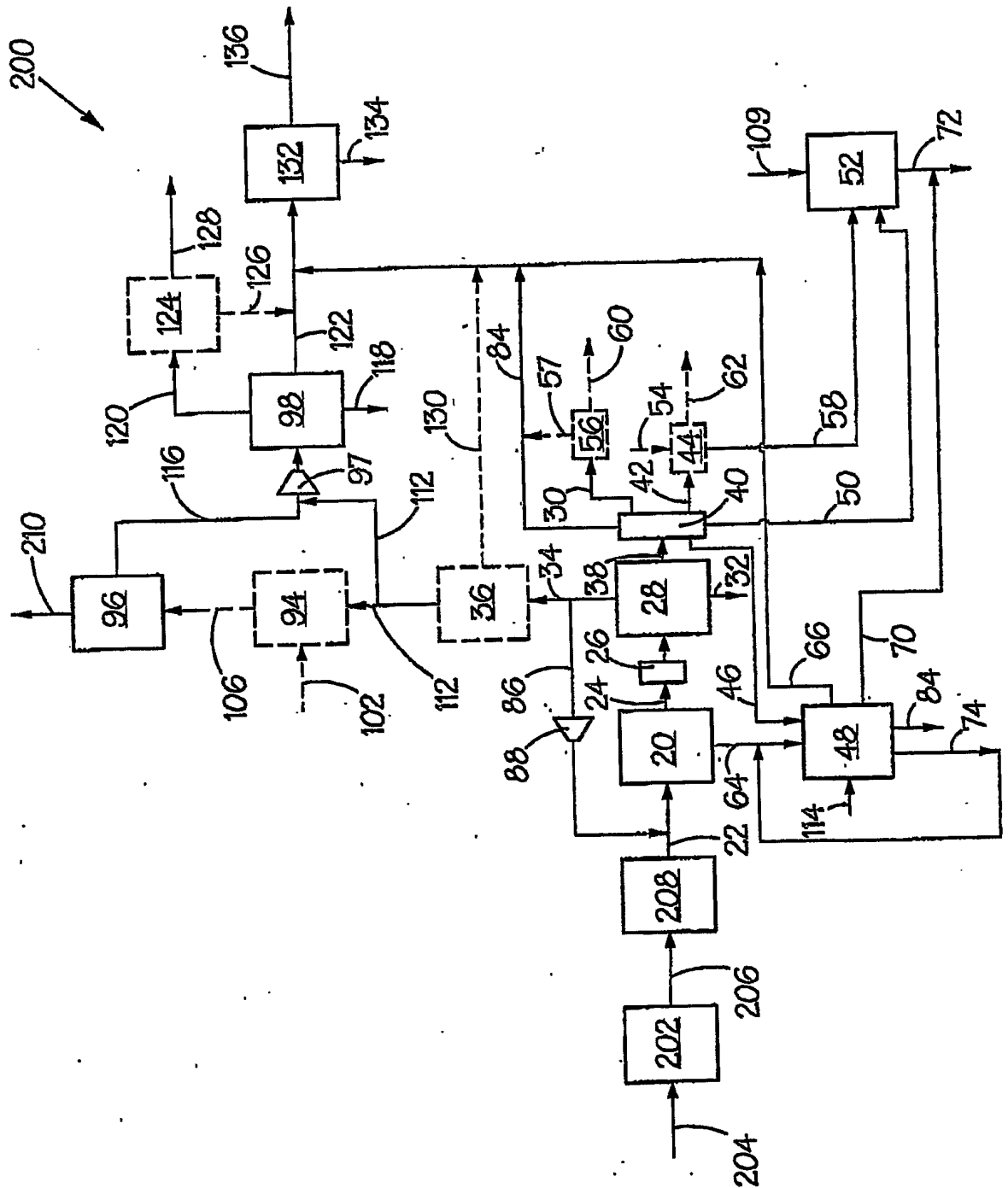


Fig 2